Non-ideal solutions

Strong deviations from ideality are shown by dissimilar substances

Raoult’s law obeyed for a close-to-pure solvent

William Henry (1775-1836) observed

Henry’s law (for a dilute solute):

\[ p_B = x_B K_B \] (e.g., gas solubility)
Ideal and real solutions: Activities

From both Raoult’s (solvent) and Henry’s laws (solute) follows:

\[ \mu_{solv}(l) = \mu_{solv}^{\ominus}(l) + RT \ln x_{solv} \]

\[ = \mu_{solv}^{\ominus}(l) + RT \ln C[solv] \]

⇒ \[ \mu_J = \mu_J^{\ominus} + RT \ln [J] \]

↓

standard chemical potential @ 1 M

The chemical potential is a measure of the ability of J to bring about physical or chemical change

BUT:

\[ \mu_J = \mu_J^{\ominus} + RT \ln a_J \]

Effective concentration = activity \[ a_J = \gamma_J[J] \]
Consequences of chemical potential changes in mixtures: Colligative properties

Freezing point depression:
\[ \Delta T_f = K_f b_B \]
frozen state

Boiling point elevation:
\[ \Delta T_B = K_B b_B \]
volatile state

Solute is insoluble in solid solvent:
Chemical Potential lowered by solute

Chemical Potential lowered by solute

Solute is not volatile:

Chemical potential vs. temperature graph showing:
- Pure liquid solvent
- Pure solid solvent
- Solvent in solution
- Depression of freezing point
- Elevation of boiling point
Phase diagrams of binary mixtures

Phase rule: \( F = C - P + 2 \)

for binary mixtures = 2

\[ p, T \]

\( F' = 2 \)

Phase \( \alpha \)

\( F' = 0 \)

Phase \( \beta \)

\[ F = 2 \]

Temperature-composition diagram for binary mixture of volatile liquids

\( p = \text{constant} \)

Temperature

Composition (mole fraction)

Temperature

Composition, \( x_A \)

Boiling point of pure B

Composition of vapour

Tie line

Boiling point of mixture

in equilibrium
Finally, as promised: Whisky distillery

Non-ideal mixtures

Fractional distillation:

High-boiling azeotrope, e.g., nitric acid/water

Low-boiling azeotrope, e.g., ethanol/water
Liquid-liquid phase diagrams of partially miscible liquids

E.g., hexane/nitrobenzene:

Upper critical solution temperature (thermal motion)

Lever rule

Amount of phase of composition $a'' = \frac{l'}{l''}$

E.g., triethylamine/water:

Lower $T_{\text{crit}}$ (complex formed)